— Chapter IX —

In this chapter, we shall begin to deal with problems in three dimensions. We shall consider the angular momentum operators associated with the orbital motion of a particle. We shall look at their commutation relations as well as their eigenvalues and eigenfunctions. We shall also consider the somewhat technical question of how we “add” angular momentum in quantum mechanics. This material is of particular importance since many of the problems which you will encounter in quantum mechanics are spherically symmetric. As a consequence, the Hamiltonian will commute with all of the angular momentum operators. As we know, we can then always find simultaneous eigenfunctions of $H$ and angular momentum operators. Many of the results which we will obtain are of greater generality. Specifically, they will also be found to apply to the intrinsic angular momentum (or “spin”) which particles can possess.

The angular momentum operators: We have repeatedly noted that angular momentum is defined classically as

$$ L = r \times p . $$

We expect that the corresponding quantum mechanical operators will therefore be given as

$$ \hat{L} = \hat{r} \times \hat{p} . $$

In other words,

$$ \hat{L}_x = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), $$

$$ \hat{L}_y = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), $$

$$ \hat{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (1) $$

Using the fundamental commutation relation $[\hat{x}, \hat{p}_x] = i\hbar$, a bit of algebra shows that the angular momentum operators satisfy the following commutation relations:

$$ [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z , $$

$$ [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x , $$

$$ [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y . \quad (2) $$

Again by analogy to classical mechanics, we can introduce an operator describing the square of the total angular momentum:

$$ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 . \quad (3) $$

Direct calculation using eqns.(2) shows that $\hat{L}^2$ commutes with each component of the angular momentum operator:

$$ [\hat{L}^2, \hat{L}_i] = 0 . \quad (4) $$

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From the definition of eqn.(3), we also note the obvious fact that

\[ \langle \hat{L}^2 \rangle \geq \langle \hat{L}_z^2 \rangle , \]  

(5)

which is always true. (We shall put this elementary observation to very good use below.)

The commutation relations of eqn.(2) warn us that we cannot hope to find simultaneous eigenfunctions of two different components of angular momentum. According to eqn.(4), we can find simultaneous eigenfunctions of \( \hat{L}^2 \) and one specific component which we take, by convention, to be \( \hat{L}_z \).

We will see in Chapter 11 that eqns.(2) and (3) remain valid when we introduce operators to describe the intrinsic spin of elementary particles. Because of this generality, we will use the symbol \( \hat{J} \) to describe a generic angular momentum — orbital or spin — below. Any result written in terms of \( \hat{L} \) will be understood to apply to orbital angular momentum only.

**Eigenvalues of the angular momentum:** We can proceed by brute force, but it is much nicer to adopt an algebraic approach similar to our earlier treatment of the harmonic oscillator. The outline of the argument (which is much as before) is as follows: We will define raising and lowering operators, \( J_{\pm} \), that change the eigenvalue of \( \hat{J}_z \) by \( \pm \hbar \), respectively. Sooner or later, the repeated application of these operators will create a state that will violate eqn.(5). As before, we shall than that there is a state of maximum acceptable \( J_z \) and that the application of \( \hat{J}_z \) to this state must give 0. This will quantize the eigenvalues. In the case of orbital angular momentum, this null equation will be a simple first-order differential equation for this maximum state. All other states can then be obtained by application of the lowering operator.

Thus, we introduce “ladder operators”,

\[
\hat{J}_+ = \hat{J}_x + i\hat{J}_y \\
\hat{J}_- = \hat{J}_x - i\hat{J}_y = \hat{J}_+^* \cdot
\]

(6)

Using eqns.(2) and (3), we construct the commutation relations

\[
[\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm
\]

\[
[\hat{J}^2, \hat{J}_\pm] = 0 \cdot
\]

(7)

The definitions also show that we can rewrite

\[
\hat{J}^2 = \hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+ \pm \hbar \hat{J}_z .
\]

(8)

We will find this result to be useful.

Now, assume that we know one eigenfunction of \( \hat{J}_z \) such that

\[
\hat{J}_z \phi_m = \hbar m \phi_m .
\]

(9)

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(At this point, we know nothing about \( m \). We shall soon show that it must either be an integer or a half integer.) It follows from the first of eqns.\((7)\) that
\[
\hat{J}_z (\hat{J}_+ \phi_m) = \hbar (m + 1)(\hat{J}_+ \phi_m) .
\]
\( (10) \)

This shows us that \( \hat{J}_+ \) raises the eigenvalue of the state by \( \pm \hbar \) and that \( \hat{J}_+ \phi_m \) is proportional to \( \phi_{m+1} \). Since \( \hat{J}_z \) commutes with \( \hat{J}^2 \), we can seek simultaneous eigenfunctions of these operators. According to the second of eqns.\((7)\), \( \phi_m \) and \( \phi_{m+1} \) have the same eigenvalue of \( \hat{J}^2 \). Call this eigenvalue \( \hbar^2 K^2 \). As indicated, \( K^2 \) must be greater than or equal to \( m^2 \). All allowed values of \( m \) thus fall in the interval \( -K \leq m \leq +K \). This means that there must exist states \( \phi_{m_{\text{max}}} \) and \( \phi_{m_{\text{min}}} \) such that
\[
\hat{J}_+ \phi_{m_{\text{max}}} = 0 \quad \text{and} \quad \hat{J}_- \phi_{m_{\text{min}}} = 0 .
\]
\( (11) \)

Using eqns.\((8)\) and \((11)\), we obtain the relations
\[
\begin{align*}
\hbar^2 K^2 &= \hbar^2 m_{\text{max}} (m_{\text{max}} + 1) \\
\hbar^2 K^2 &= \hbar^2 m_{\text{min}} (m_{\text{min}} - 1) .
\end{align*}
\]
\( (12) \)

These two equations tell us that
\[
m_{\text{max}} (m_{\text{max}} + 1) = m_{\text{min}} (m_{\text{min}} - 1) ,
\]
which indicates that
\[
m_{\text{max}} = -m_{\text{min}} \equiv j .
\]
\( (13) \)

(The other solution to this quadratic equation is ruled out since \( m_{\text{max}} \) and \( m_{\text{min}} \) must have opposite signs.) But we must be able to get from \( +j \) to \( -j \) by a number of applications of \( \hat{J}_- \). Thus, \( 2j \) must be an integer; \( j \) can either be an integer or a half integer.

To summarize, we have found that
\[
\begin{align*}
\hat{J}^2 |jm \rangle &= \hbar^2 j (j + 1) |jm \rangle \\
\hat{J}_- |jm \rangle &= \hbar m |jm \rangle 
\end{align*}
\]
\( (14) \)

where \( j \) is an integer or half integer and \( m \) runs in integer steps from \( -j \) to \( +j \).

I emphasize that we still have not found the eigenfunctions.

**Construction of the eigenfunctions:** Let us first agree to work in spherical polar coordinates defined by
\[
\begin{align*}
x &= r \sin \theta \cos \phi \\
y &= r \sin \theta \sin \phi \\
z &= r \cos \theta .
\end{align*}
\]
\( (15) \)

Using eqns.\((1)\) and considerable algebra, we can find a representation of the raising and lowering operators for orbital angular momentum as
\[
\hat{L}_\pm = \hbar \cot \phi \left( i \cot \theta \frac{\partial}{\partial \phi} \pm \frac{\partial}{\partial \theta} \right) .
\]
\( (16) \)
We also find that
\[ \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}. \]  
(17)

Let try to find the state of “maximum weight”, \(|\ell \ell\rangle\) which has the property that
\[ \hat{L}_+ |\ell \ell\rangle = 0. \]

This should be an easy equation to solve. All other states can then be constructed by the mechanical procedure of repeatedly apply \(\hat{L}_-\) to this state. A little effort reveals that the solution to this equation must be of the form
\[ \sin^\alpha \theta e^{i \alpha \phi}. \]

Inspection of eqn.17 shows that \( \alpha = \ell \). Thus,
\[ |\ell \ell\rangle \sim \sin^\ell \theta e^{i \ell \phi}. \]  
(18)
The “\( \sim \)” indicates that these states are not normalized. As we have seen in generality, \( \ell \) must be either an integer or a half integer.

We are not quite finished. We certainly wish our eigenfunctions to be single valued.\(^1\) The form of eqn.(18) reveals that this rules out the choice \( \ell \) equal to a half integer.\(^2\)

\textbf{Spherical harmonics:} If we actually work out the general form of \(|\ell m\rangle\), we discover that these angular functions (called “spherical harmonics”) can be written as
\[ Y_{\ell}^m(\theta, \phi) = \left[ \frac{2\ell + 1}{4\pi} \frac{(\ell - m)!}{(\ell + m)!} \right]^{1/2} P_{\ell}^m(\cos \theta) e^{im\phi} \]  
(19)
where \( P_{\ell}^m \) is an associated Legendre polynomial. The angular functions in eqn.(19) are normalized to 1.\(^3\) These functions reduce to the ordinary Legendre polynomials, \( P_{\ell} \) when \( m = 0 \).

The Legendre polynomials, \( P_{\ell}(z) \), are orthogonal on the interval \(-1 \leq z \leq +1\) according to
\[ \int_{-1}^{+1} dz P_{\ell}(z) P_{\ell'}(z) = \frac{2}{2\ell + 1} \delta_{\ell \ell'}. \]

They can be obtained from the generating function
\[ [1 - 2zs + s^2]^{-1/2} = \sum_{\ell=0}^\infty s^\ell P_{\ell}(z). \]  
(20)

This generating function makes it clear that \( P_{\ell}(z) \) is a polynomial of order \( \ell \) in \( z \). Thus, the Legendre polynomials have a one-to-one correspondence with \( z^\ell \). This means that the Legendre functions are complete and span the Hilbert space of functions which are square integrable on the interval \(-1 \leq z \leq +1\).

\(^1\)In other words, \( \psi_{\ell \ell}(\theta, \phi + 2\pi) = \psi_{\ell \ell}(\theta, \phi) \).
\(^2\)We shall reserve half integer values of \( \ell \) to describe the intrinsic (i.e., non-orbital) angular momentum of certain elementary particles. More about this later.
\(^3\)The weight for normalization integrals is, of course, \( d\Omega = \sin\theta d\theta d\phi \).
If we need the associated Legendre polynomials, we can get them from the definition
\[ P^m_\ell(z) = (-1)^m (1 - z^2)^{m/2} \frac{d^m}{dz^m} P_\ell(z) . \] (21)
This result is evidently consistent with eqn.(18) when \( m = \ell \).

Why all the fuss?: There is a good reason for being so thorough in the above discussion. The Hamiltonian for every spherically symmetric problem will always commute with \( \hat{L}_z \).\(^4\) Thus, we can always find simultaneous eigenfunctions of \( \hat{H}, \hat{L}_z^2, \) and \( \hat{L}_z \). Further, the eigenfunctions of spherically symmetric problems can always be written in terms of the spherical harmonics as
\[ \psi(r, \theta, \phi) = R(r) Y^m_\ell(\theta, \phi) . \]
Thus, at one stroke, we have solved two-thirds of the problem of a particle in a spherical potential once and for all!

Coupling of angular momentum: Imagine that we have two independent and non-interacting particles. Each particle has three angular momentum operators which obey the commutation relations of eqns.(2). Since the particle are independent, we know that
\[ [\hat{L}_{1i}, \hat{L}_{2j}] = 0 \] (22)
for all \( i \) and \( j \). One complete set of four mutually commuting operators is the obvious \( \hat{L}_1^2, \hat{L}_{1z}, \hat{L}_2^2, \) and \( \hat{L}_{2z} \). There is another possibility. We can define total angular momentum operators as
\[ \hat{L}_\text{total} = \hat{L}_1 + \hat{L}_2 . \] (23)
We can similarly define raising and lowering operators, \( \hat{L}_z\text{\_{\text{total}}} \), of the total angular momentum. It is then easy to show than another mutually commuting set of four operators is \( \hat{L}_1^2, \hat{L}_2^2, \hat{L}_\text{\_{\text{total}}}^2, \) and \( \hat{L}_z\text{\_{\text{total}}} \). Thus, we can classify eigenfunctions either by \( |\ell_1 m_1 \ell_2 m_2 \rangle \) or by \( |\ell_1 \ell_2 \ell m \rangle \). Since each of the two bases is complete and orthogonal, there is a simple linear transformation between them. For example,
\[ |\ell_1 \ell_2 \ell m \rangle = \sum_{m_1 + m_2 = m} (\ell_1 m_1 \ell_2 m_2 |\ell_1 \ell_2 \ell m \rangle |\ell_1 m_1 \ell_2 m_2 \rangle ) . \] (24)
The coefficients in this transformation,\(^5\) \( (\ell_1 m_1 \ell_2 m_2 |\ell_1 \ell_2 \ell m \rangle \), are known as “Clebsch-Gordan coefficients.” The constraint on the sum in eqn.(24) follows immediately from the definition of eqn.(23).

Unitary transformations: The transformations between two alternate sets states each of which is complete, orthogonal, and normalized are somewhat special. To see this, use a (finite) matrix notation to write
\[ |i \rangle = U_{ia} |a \rangle \quad \text{and} \quad |a \rangle = (U^{-1})_{ai} |i \rangle . \] (25)
\(^4\)Recall that the \( \hat{L}_i \) are the generators of infinitesimal rotations.
\(^5\)Which are simply numbers!
(Here, I have used the familiar matrix convention that there is an implied sum whenever an index is repeated.) From the first of these equations, we see that
\[ \langle i | i' \rangle = U_{i' \lambda}^* U_{i \alpha} \langle a | a' \rangle . \] (26)

Given the orthogonality of the states and the definition of the Hermitean adjoint of a matrix, the eqn.(26) reduces to the statement that
\[ U_{i \alpha}^\dagger U_{i' \alpha'} = \delta_{i' \alpha'} . \] (27)

In other words, the Hermitean adjoint of \( U \) is equal to its inverse,
\[ U^\dagger = U^{-1} . \]

Such matrices are called “unitary matrices.”

\textit{The allowed eigenvalues of \( \hat{J}_z \text{total} \):} Let us think of a system with fixed \( j_1 \) and \( j_2 \). The state of “maximum weight” has \( m = j_1 + j_2 \). Clearly, application of \( \hat{J}_z \text{total} \) to this state will give 0. Hence, this state has \( j = j_1 + j_2 \). There are 2 states with \( m = j_1 + j_2 - 1 \). One of these is evidently the state \( |j_1, j_2 j - 1 \rangle \). The orthogonal combination evidently vanishes when \( \hat{J}_z \text{total} \) is applied to it. Thus, it must be the state \( |j_1, j_2 j - 1 j - 1 \rangle \). At \( m = j_1 + j_2 - 2 \), there are three states. The third state must vanish under application of the raising operator and must therefore be \( |j_1, j_2 j - 2 j - 2 \rangle \). This pattern continues until we reach \( m = j_1 - j - 2 \).

From there down to \( m = 0 \), the number of states remains constant at \( 2j_2 + 1 \). Thus, we find precisely one state for each value of \( j \) between
\[ |j_1 - j_2| \leq j \leq j_1 + j_2 . \] (28)

This result is independent of whether \( j_1 \) and \( j_2 \) are integers or half integers. (I understand that this argument is a little dense. But it is simple. If you carry out this scheme for a couple of choices of \( j_1 \) and \( j_2 \), all will become clear!)

One check on this scheme comes from the fact that
\[ \sum_{j = |j_1 - j_2|}^{j_1 + j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1) . \]

\textit{Calculating Clebsch-Gordan coefficients:} In order to actually calculate the Clebsch-Gordan coefficients appearing in eqn.(24), it is useful to know an additional fact about the raising and lower operators. Specifically,
\[ \hat{J}_\pm \hat{J}_\pm = \hat{J}^2 - \hat{J}_z^2 \mp \hbar \hat{J}_z . \] (29)

This allows us to express the action of the raising and lowering operators in terms of correctly normalized kets:
\[ \hat{J}_\pm |jm \rangle = [(j \mp m)(j \pm m + 1)]^{1/2} |jm \pm 1 \rangle . \] (30)

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\(^6\)\( U^\dagger = (U^T)^* \).

\(^7\)I assume that \( j_1 \geq j_2 \).
(Note that eqn.(30) vanishes when \( \hat{J}_+ \) acts on \( |jj\rangle \) and when \( \hat{J}_- \) acts on \( |j-j\rangle \). This is correct.)

First, construct the Clebsch-Gordan coefficients for the state \( |j_1,j_2,jj\rangle \) by assuming that the state has the structure of eqn.(24). Applying the raising operator to this state gives 0. Thus, apply the raising operator \( \hat{J}_{1+} + \hat{J}_{2+} \), to the right side of eqn.(24), use eqn.(30), and equate the result to 0. This gives a particularly elementary set of linear equations which can be solved “by inspection.” The Clebsch-Gordan coefficients for this state emerge following normalization. For other states, start again with the (now known) state \( |j_1,j_2,jj\rangle \) written in the form of eqn.(24). Apply \( \hat{J}_{\text{total} -} \) to the left of this equation using eqn.(30) and applying \( \hat{J}_{1-} + \hat{J}_{2-} \) to the right side of this equation (again using eqn.(30).) The correctly normalized state \( |j_1,j_2,jj - 1\rangle \) (and hence the Clebsch-Gordan coefficients) emerge immediately. Repeated applications of the lowering operator in this manner give all of the Clebsch-Gordan coefficients.

Again, it is more complicated to explain this procedure than it is to actually apply it. Try this scheme for a couple of choices of \( j_1 \) and \( j_2 \), and you will understand it.\(^8\)

More than two particles: The complete classification of the angular momentum states of more than two particles follows from the repeated application of the above rules. The most difficult part is getting a complete set of operators. For three particles, for example, we know that we can completely classify the states as

\[
|j_1m_1j_2m_2j_3m_3\rangle .
\]

This means that we need six mutually commuting operators. One (of many) such sets allows us to construct states as

\[
|(j_1j_2)J_{12}j_3JM\rangle .
\]

This means: Couple \( j_1 \) and \( j_2 \) to angular momentum \( J_{12} \). Then couple \( J_{12} \) and \( j_3 \) to total angular momentum \( J \) and its z component \( M \). This can be accomplished by the repeated application of eqn.(23) as

\[
|(j_1j_2)J_{12}j_3JM\rangle = \sum_{m_1+m_2=M_{12}} \sum_{M_{12}+m_3=M} \left( j_1m_1j_2m_2|j_1j_2J_{12}M_{12}\rangle \right) \left( J_{12}M_{12}j_3m_3|J_{12}j_3JM\rangle |j_1m_1j_2m_2j_3m_3\rangle \right).
\]

This procedure is tedious but well-suited to computer evaluation.

The case of four or more particles follows by analogy.

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\(^8\)Conversely, if you do not actually try to construct the Clebsch-Gordan coefficients, it is virtually guaranteed that you will not understand what is going on! Do it!
In this chapter we shall deal with some problems in three dimensions. We shall first see how to write the Schrödinger equation in polar coordinates. We shall consider the problem of a particle in a constant magnetic field. We shall see how to reduce the problem of two particles interacting through a potential to an effective one-particle problem. Finally, we will solve the hydrogen atom problem. Throughout, we will make use of the angular momentum eigenfunctions and eigenvalues found in Chapter IX.

A free particle in Cartesian coordinates: There is nothing much new here. As usual, we write
\[ \hat{p} = -i\hbar \nabla \]
and
\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 . \]
The corresponding Schrödinger equation is separable in Cartesian coordinates. By the usual arguments, we can see that
\[ \psi(x, y, z) = X(x)Y(y)Z(z) . \]
It follows immediately that
\[ \psi_k(r, t) = \frac{1}{(2\pi)^{3/2}} e^{i(k \cdot r - \omega t)} . \]
Here, the three quantum numbers of the state are the components of \( k \). The energy is \( E = \hbar^2 k^2 / 2m = \hbar \omega \).

A free particle in polar coordinates: Let us make use of standard (classical) vector identities to write
\[ L^2 = (\mathbf{r} \times \mathbf{p})^2 = r^2 p^2 - (\mathbf{r} \cdot \mathbf{p})^2 . \quad (1) \]
This tells us that the classical Hamiltonian for a free particle is
\[ H = \frac{p^2}{2m} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} \quad (2) \]
where
\[ p_r \equiv \frac{1}{r}(\mathbf{r} \cdot \mathbf{p}) . \quad (3) \]
Our expectation is that eqn.(2) will remain valid in quantum mechanics if we simply replace \( p_r \) and \( L^2 \) by the corresponding quantum mechanical operators. We have already constructed \( \hat{L}_i \) and \( \hat{L}^2 \) in Chapter IX. (See eqn.(1) there.) It is apparent from their form that both the \( \hat{L}_i \) and \( \hat{L}^2 \) are Hermitean operators. Since \( p_r \) will involve a combination of position and momentum operators, we will have to be a little careful to guarantee that it is Hermitean.
**Infinitesimal rotations:** Imagine that we have a function \( f(r) \) and that we would like to rotate this function through some small angle about a specified axis. This can be accomplished by the replacement

\[
r \rightarrow r + \delta \phi \times r .
\]

If \( f \) happens to be an isotropic function, \( f(r) \), it will be invariant under rotations. Eqn.(4) realizes this since

\[
(r + \delta \phi \times r)^2 = r^2 + 2r \cdot (\delta \phi \times r) + \mathcal{O}(\delta \phi^2) = r^2 + \mathcal{O}(\delta \phi^2) .
\]

Given the explicit form of the operators \( \hat{L}_i \), we can verify that the quantum mechanical operator which produces infinitesimal rotations is simply

\[
\hat{R}_{\delta \phi} = 1 + i \delta \phi \cdot \hat{L}/\hbar .
\]

As we have seen before, invariance of the Hamiltonian under rotations implies that the Hamiltonian commutes with the generators of the rotation (i.e., the angular momentum operators). This can, of course, also be verified using the explicit form of the angular momentum operators.

**The radial momentum:** Using the classical form of eqn.(3), it is tempting to write the radial momentum as

\[
\frac{1}{r}(\hat{x}\hat{p}_x + \hat{y}\hat{p}_y + \hat{z}\hat{p}_z) .
\]

Unfortunately, this form is not Hermitean. So a better guess would be half of the sum of eqn.(7) plus its Hermitean adjoint. Thus,

\[
\hat{p}_r = \frac{1}{2} \left( \frac{1}{r} \hat{r} \cdot \hat{p} + \hat{p} \cdot \hat{r} \frac{1}{r} \right) .
\]

Working out the form of eqn.(8) requires nothing more than the usual forms of the momentum operators. Some effort reveals that

\[
\hat{p}_r = -i\hbar \frac{1}{r} \frac{\partial}{\partial r} r .
\]

Using eqn.(1) above and this form for \( \hat{p}_r \), we can now write down the quantum mechanical Hamiltonian for a free particle in polar coordinates. It has the form

\[
\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2mr^2} .
\]

**The Laplacian:** I always have a hard time remembering the Laplacian in polar coordinates. It is easier to remember the form of the gradient operator which is

\[
\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} .
\]
(Here the “hat” simply stands for an ordinary unit vector.) The form of the Laplacian comes immediately by writing the integral
\[ \int d^3r \nabla f \cdot \nabla g = - \int d^3r f \nabla^2 g \]
which follows by one integration by parts. The only other thing you need to recall is that
\[ d^3r = r^2 \sin \theta \, dr \, d\theta \, d\phi \, . \]
One then finds
\[ \nabla^2 = \left( \frac{1}{r} \frac{\partial}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \, . \quad (11) \]
This is a check that we have done things right since we can also write eqn.(10) in the expected form
\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 \, . \]

Since \([\hat{H}, \hat{L}_i] = 0\), we can seek solutions of the Schrödinger equation which are simultaneous eigenfunctions of \(\hat{H}, \hat{L}_z\), and \(\hat{L}_x\). Further, the form of eqn.(11) reveals that the Schrödinger equation is again separable in polar coordinates. Thus, wave functions will have the form
\[ \psi(r, \theta, \phi) = R(r) Y_{\ell m}^m(\theta, \phi) \, . \quad (12) \]
This makes our task simpler since we already know all about the spherical harmonics. Note that these remarks remain valid if we add any spherically symmetric potential, \(V(r)\), to the problem. Our task, in general, is only to solve the resulting radial equation in order to determine \(R(r)\) and the corresponding energy eigenvalues.

**Solutions for the free particle:** For a free particle, the radial equation becomes
\[ \left[ -\frac{1}{r} \frac{d^2}{dr^2} r^2 + \frac{\ell(\ell+1)}{r^2} \right] R_{\ell k}(r) = k^2 R_{\ell k}(r) \quad (13) \]
where \(E = \hbar^2 k^2 / 2m\) as usual. We note that the second term on the left has a simple interpretation as a “centrifugal barrier” which is familiar from classical mechanics. This barrier creates a classically forbidden region for sufficiently small \(r\) which will force the wave function to vanish as \(r \to 0\) for all \(\ell \neq 0\).

The solutions to eqn.(13) are familiar and even elementary functions. They are the “spherical Bessel functions” \(j_\ell(kx)\) and \(n_\ell(kx)\).\(^9\) We can specify them completely by noting that
\[ j_0(x) = \frac{\sin x}{x} \quad \text{and} \quad n_0(x) = -\frac{\cos x}{x} \]
\[ j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \quad \text{and} \quad n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x} \quad (14) \]

\(^9\)To be precise, the first of these is a spherical Bessel function; the second is a spherical Neumann function.

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and that both of these functions satisfy the recursion relation
\[ f_{\ell-1} + f_{\ell+1} = (2\ell + 1) f_{\ell}/x . \] (15)

In the limit of small \( x \), these equations show that \( j_\ell(x) \sim x^\ell \) and \( n_\ell(x) \sim 1/x^{\ell+1} \). Since \( \ell \) must be a non-negative integer, it is clear that \( j_\ell(x) \) is regular at the origin while \( n_\ell(x) \) is irregular (i.e., divergent). For a free particle, we are not interested in the divergent solution. Thus, our plane wave in three dimensions can be written as
\[ |k\ell m\rangle = j_\ell(kr) Y_\ell^m(\theta, \phi) \] (16)

with the normalization
\[ \langle k\ell m|k'\ell' m'\rangle = \delta_{mm'} \delta_{\ell \ell'} \frac{\pi}{2k^2} \delta(k - k') . \] (17)

Of course, \( k \) can be any real number. Since the Hamiltonian is Hermitian, it comes as no surprise that these eigenfunctions are orthogonal. They can also be shown to be complete. That is, they span the Hilbert space of all functions which are square integrable on the interval \( 0 \leq r \leq +\infty \) with weight \( r^2 \).

**Plane waves and spherical waves:** Any standard mathematical text on special functions reveals that we can expand a plane wave in the spherical waves of eqn.(16) as
\[ e^{ikr} = \sum_{\ell m} 4\pi i^\ell |Y_\ell^m(\alpha, \beta)|^* |k\ell m\rangle \] (18)

where we label \( k \) by its polar coordinates \( (k, \alpha, \beta) \). If we have a plane wave, measurement of \( L^2 \) and \( L_z \) will return the value \( \ell \) and \( m \) with probability
\[ (4\pi)^2 |Y_\ell^m(\alpha, \beta)|^2 \]
and will, of course, place the system in the state \( |k\ell m\rangle \).

**A classical particle in a magnetic field:** The classical force on a charged particle in an electric and magnetic field is given by
\[ \mathbf{F} = e \left[ \mathbf{E} + \frac{1}{c}(\mathbf{v} \times \mathbf{B}) \right] . \] (19)

It is conventional to write the electric and magnetic fields in terms of scalar and vector potentials so that
\[ \mathbf{E} = \nabla \phi \quad \text{and} \quad \mathbf{B} = \nabla \times \mathbf{A} . \] (20)

The corresponding classical Lagrangian is
\[ L = \frac{1}{2}m\dot{q}^2 - e\phi + \frac{e}{c} \mathbf{A} \cdot \dot{\mathbf{q}} . \] (21)

It can be verified directly that eqn.(21) leads to eqn.(20) by using the methods described in Chapter I. As always, the momentum which is canonically conjugate to \( q \) can be obtained as
\[ p = \frac{\partial L}{\partial \dot{q}} . \]
This gives us
\[ \mathbf{p} = m\dot{\mathbf{q}} + \frac{e}{c} \mathbf{A}. \] (22)

The classical Hamiltonian can now be written in terms of \( q \) and \( p \) as
\[ H = \frac{1}{2m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + e\phi(x). \] (23)

Following the Correspondence Principle, we expect that the quantum mechanical Hamiltonian will result from replacing \( \mathbf{p} \) by \( \hat{\mathbf{p}} \). This expectation is correct.

A particle in a constant magnetic field: The definition of the vector potential, eqn.(20), makes it clear that one way\(^{10}\) to write a constant magnetic field in the direction \( \hat{z} \) is \( A_x = -yB, A_y = A_z = 0 \). Eqn.(23) then shows us that
\[ \hat{H} = \frac{1}{2m} \left[ \left( \hat{p}_x + \frac{eB}{c} \right)^2 + \hat{p}_y^2 + \hat{p}_z^2 \right]. \] (24)

Evidently, the coordinates \( x \) and \( z \) are cyclic. Thus, \( \hat{H} \) commutes with both \( \hat{p}_x \) and \( \hat{p}_z \), and we can find simultaneous eigenfunctions of these three operators. The Schrödinger equation is again separable with solutions of the form
\[ \psi(x,y,z) = f(y)\phi_{k_x k_z}(x,z) \] (25)

with
\[ \phi_{k_x k_z}(x,z) = e^{ik_x x + k_z z} \] (26)

for any real values of \( k_x \) and \( k_z \). The remaining equation for \( f(y) \) has the form
\[ \left[ \hat{p}_y^2 + \frac{1}{2} K(y - y_0)^2 \right] f(y) = \left( E - \frac{\hbar^2 k_z^2}{2m} \right) f(y). \] (27)

Here, I have introduced the definitions
\[ y_0 \equiv -\frac{\hbar k_x}{eB} \quad \text{and} \quad K \equiv \left( \frac{eB}{mc} \right)^2 = \Omega^2 \]

where \( \Omega \) is the classical frequency (i.e., the “cyclotron frequency”) describing the rotation of a charged particle in this magnetic field. Evidently, eqn.(27) is a one-dimensional harmonic oscillator problem which we have already solved.

The energy eigenvalues can be written by inspection as
\[ E_n = \hbar\Omega(n + 1/2) + \frac{\hbar^2 k_z^2}{2m}. \] (28)

These states are known as “Landau levels.” Eqn.(28) comes as a bit of a surprise. We are in three dimensions and should have expected three quantum numbers to label the states exactly. This is correct since we can label our

\[ ^{10}\text{There are infinitely many other ways to write this. This is known as "gauge invariance."} \]
states uniquely as $|nk_xk_z\rangle$. However, the energy is a function of only two of these quantum numbers! This, implies an infinite degeneracy of levels.\(^\text{11}\)

Because of the large degeneracy just noted, there is considerable flexibility in the way we describe the eigenfunctions of the system and consequently in the qualitative description of the motion. There is a simple classical analogue of this degeneracy. Classically, we expect to find free motion in the $z$ direction and circular motion in the $xy$ plane with a frequency $\omega$. The center of this circle can be located anywhere in the $xy$ plane. These is the classical “degeneracy.” The quantity $y_0$ appearing in eqn.(27) corresponds to the $y$ coordinate of the center of the circle. The quantity

$$x_0 = c\hat{p}_y/eB + \hat{x}$$

represents the $x$ coordinate of the circle (i.e., the operator $x_0$ commutes with the Hamiltonian. Recalling that

$$y_0 = c\hat{p}_x/eB ,$$

we see that we cannot determine $x_0$ and $y_0$ simultaneously (since the corresponding operators do not commute.)\(^\text{12}\) We could certainly make minimum uncertainty wave packets with $x_0$ and $y_0$ maximally well determined. Such wave packets mimic the spiral motion of a classical with increasing accuracy as $\hbar \to 0$.

**Relative and center of mass coordinates:** Consider the classical Hamiltonian

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|r_1 - r_2|) .$$

We know that we can greatly simplify this problem by working with relative and center of mass coordinates defined as

$$r = r_2 - r_1 \quad \text{and} \quad R = \frac{m_1r_1 + m_2r_2}{m_1 + m_2}$$

$$p = \frac{m_2p_1 - m_1p_2}{m_1 + m_2} \quad \text{and} \quad P = p_1 + p_2 .$$

(30)

In these relative and center of mass coordinates, eqn.(29) becomes

$$H = \frac{P^2}{2M} + \left[ \frac{p^2}{2\mu} + V(r) \right] ,$$

where I have used the usual definition of total and reduced masses, $M = m_1 + m_2$ and $\mu = m_1m_2/(m_1 + m_2)$. Evidently, the center of mass coordinate $R$ is cyclic.

\(^{11}\)In infinite space. If we put the system in a large box, $k_z$ will be quantized and we will have a (presumably large) discrete degeneracy of each state.

\(^{12}\)It is easy to verify the corresponding classical expressions $x_0 = cm_2y/eB + x$ and $y_0 = -cm_1x/eB + y$ when $x(t)$ and $y(t)$ are in circular motion. The present expressions arise when we eliminate $x$ and $y$ in favor of the corresponding canonical momentum.
We can make the transformations of eqn.(30) quantum mechanically. The coordinates and the conjugate momenta satisfy the usual commutation rules. The problem becomes separable in relative and center of mass coordinates (e.g., eigenfunctions become products of functions of $\mathbf{R}$ and $r$), and the center of mass eigenfunctions are simply plane waves. The center of mass momentum is conserved since the corresponding operator commutes with $\hat{H}$. Since the problem posed is spherically symmetric, the Schrödinger equation in the relative coordinate is separable in polar coordinates. (The angular eigenfunctions are simply spherical harmonics.) Thus, our original problem in six disgusting degrees of freedom reduces to a sequence of one-dimensional problems in $r$ (one for each angular momentum, $\ell$):

$$\left[ \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} + V(r) \right] R(r) = ER(r) . \quad (32)$$

Eqn.(32) has the structure of a problem in one Cartesian dimension with the effective potential

$$V_{\text{eff}} = V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} . \quad (33)$$

Such effective problems are also familiar from classical mechanics.

The hydrogen atom: After all of these weeks of work, we have finally reached 1913 and the problem of hydrogenic atoms (with one electron and a nucleus of charge $+Ze$.) This time we shall do it properly by solving the Schrödinger equation. The Hamiltonian has the form

$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{\ell}^2}{\ell^2} - \frac{Ze^2}{r} . \quad (34)$$

Note that the reduced mass of the hydrogen atom is very close to the electron mass. Since $V(r) \to 0$ as $r \to \infty$, we expect that there will be a continuum of solutions with $E > 0$. There may also be a discrete set of localized, bound states solutions with $E < 0$.\(^{13}\) We will concern ourselves with the bound state solutions. We turn immediately to the radial Schrödinger equation, eqn.(32), and use the notation $u(r) = rR(r)$. We find

$$\left( \frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{r^2} - \frac{2\mu Ze^2}{r\hbar^2} + \frac{2\mu |E|}{\hbar^2} \right) u = 0 . \quad (35)$$

We now introduce a lot of notation to make this equation look cleaner.

$$\rho = 2\kappa r \quad \frac{\hbar^2 \kappa^2}{2\mu} = |E|$$

$$\chi^2 = \left( \frac{Z}{\kappa a_0} \right)^2 = \frac{Z^2 R}{|E|}$$

\(^{13}\)As we shall see, there are infinitely many such bound states.
\[ \mathcal{R} = \frac{\hbar^2}{2\mu a_0^5} \quad a_0 = \frac{\hbar^2}{\mu e^2} . \]  

The only thing worth noting here is that \( \mathcal{R} \) is called the Rydberg constant and \( a_0 \) is the Bohr radius. With this notation, eqn.(35) can be written as

\[ \frac{d^2u}{d\rho^2} - \frac{\ell(\ell + 1)}{\rho^2}u + \left( \frac{\lambda}{\rho} - \frac{1}{4} \right)u = 0 . \]  

We will solve this equation by brute force (just as we did with the harmonic oscillator.) The strategy is clear. We first extract the asymptotic form of the wave function. We treat the remainder of the solution as a power series and find a recursion relation for the coefficients. Inspection of this series will reveal a divergence (for large \( r \)) which will, in general, beat the convergent asymptotic form. To avoid this, we consider only the localized solutions which result when this series expansion contains a finite number of terms. This provides the discrete eigenvalues (and the corresponding eigenfunctions.) All we have to do is implement this strategy.

For large \( \rho \), eqn.(37) reduces to

\[ \frac{d^2u}{d\rho^2} = \frac{u}{4} . \]

The physically acceptable solution is simply

\[ u \sim \exp(-\rho/2) . \]

Similarly, for \( \rho \to 0 \), the centrifugal term dominates. Then, we must have

\[ u \sim \rho^{\ell+1} . \]

Thus, we seek solutions of the form

\[ u = F(\rho)\rho^{\ell+1}e^{-\rho/2} \]  

with

\[ F(\rho) = \sum_{n=0}^{\infty} c_m \rho^n . \]  

First substitute eqn.(38) into eqn.(37) to get an equation for \( F(\rho) \). Then use the form of eqn.(39). Equate the coefficients of powers of \( \rho \) to find the recursion relation

\[ c_{m+1} = \frac{m + \ell + 1 - \lambda}{(m + 1)(m + 2\ell + 2)} c_m . \]  

The series has an asymptotic behaviour,

\[ c_{m+1}/c_m = 1/m , \]

which is identical to the expansion of the divergent exponential, \( e^\rho \). In general, this term will dominate the convergent exponential in eqn.(39), and the wave
function will diverge for large $\rho$. The only way to prevent this is to choose $\lambda$
(and, hence, the energy) so that the series truncates after a finite number of
terms. In other words, we require that

$$\lambda = n \quad n = 1, 2, 3, \ldots$$

(41)

This means that we have now quantized the energies at the values

$$E_n = -\frac{Z^2 R}{n^2}.$$  

(42)

This is Bohr’s famous result, now obtained using “modern” quantum mechanics.
It is experimentally correct.

The wave functions: We have written the hydrogenic wave functions as

$$u = F(\rho) \rho^{\ell+1} e^{-\rho/2}.$$ 

The $F_{n\ell}(\rho)$ we have found are actually known special functions — the Laguerre
polynomials. Specifically,

$$F_{n\ell}(\rho) = L_{n-\ell-1}^{2\ell+1}(\rho).$$  

(43)

The Laguerre polynomials satisfy the orthogonality relation

$$\int_0^{\infty} dz e^{-z} z^q \, L_p^q L_p^{q'} = \frac{[(p+q)!]^3}{p!} \delta_{pp'}.$$  

(44)

These functions can be obtained from the relations

$$L_p^q(z) = e^z \frac{d^p}{dz^p} \left( z^p e^{-z} \right)$$

$$L_p^q(z) = (-1)^q \frac{d^q}{dz^q} \left[ L_{p+q}^0(z) \right].$$  

(45)

Positive energy states: Note that we have discussed only the bound states
of hydrogen with $E < 0$. Since $V(r) \to 0$ as $r \to \infty$, there must be a continuum
of states with (any) $E > 0$ which describe the scattering states on a proton (or
charged nucleus) and a single electron. We will not discuss these states in any
detail.

Degeneracies of the hydrogenic states: Note from eqn.(42) that the energy
of the state $|n\ell m\rangle$ depends only on the principal quantum number, $n$. This
implies a considerable degeneracy. Specifically, there are $2\ell + 1$ values of $m$
for each value of $\ell$. Further, $\ell$ can range from $0 \leq \ell \leq (n - 1)$. This implies that

the degeneracy of $E_n = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2.$  

(46)

This degeneracy causes no problems since the quantum numbers $|n\ell m\rangle$ provide
a complete classification of all states.
More complicated atoms: We can provide an approximate description of atoms with more electrons by invoking the Aufbauprinzip which states that each distinct hydrogenic state can hold two electrons at most. Then, we describe atomic ground state wave functions by “filling” the lowest energy hydrogenic states. This is only an approximation because it neglects the Coulomb repulsion between electrons. Any time we encounter a “closed” shell of electrons, we expect to find an energetically (and therefore chemically) stable atom. Thus, helium has the closed shell structure of 1s\(^2\) and neon has the closed shell structure of 1s\(^2\)2s\(^2\)2p\(^6\). These elements are known to be chemically inert.

Molecular binding and orbit hybridization: We can consider the problem of minimizing the energy of two atoms, each of which has a partially filled outermost shell of electrons. We now have the very difficult problem of minimizing the energy due to the many pairwise interactions between all of the electrons plus their nuclei. In this task, it is helpful to note that, e.g., the four orbits with \(n = 2\) are degenerate in energy. We can thus make linear combinations of these orbits (called “hybrid” orbitals) in order to minimize the total energy. There are three important combinations which are worth mentioning. We shall consider only the 2s2p shell which is relevant for the chemistry of atoms near carbon.

The combinations
\[
\begin{align*}
\phi_{2px} &= -\frac{1}{\sqrt{2}}(\phi_{211} - \phi_{21-1}) \sim xe^{-r/2a_0} \\
\phi_{2py} &= \frac{1}{\sqrt{2}}(\phi_{211} + \phi_{21-1}) \sim ye^{-r/2a_0} \\
\phi_{2pz} &= \phi_{210} \sim ze^{-r/2a_0}.
\end{align*}
\]

These orbits are shape like a cylindrically symmetric “8” with the symmetry axes along the \(x\), \(y\), and \(z\)-axis, respectively. The angle between the “lobes” of these wave functions is 90°. This accounts for the angle between the bonds in H\(_2\)O.

The so-called \(sp^3\) hybrids have the form
\[
\begin{align*}
\psi_1 &= \frac{1}{2}(\phi_{2s} + \phi_{2px} + \phi_{2py} + \phi_{2pz}) \\
\psi_2 &= \frac{1}{2}(\phi_{2s} - \phi_{2px} - \phi_{2py} + \phi_{2pz}) \\
\psi_3 &= \frac{1}{2}(\phi_{2s} + \phi_{2px} - \phi_{2py} - \phi_{2pz}) \\
\psi_4 &= \frac{1}{2}(\phi_{2s} - \phi_{2px} + \phi_{2py} - \phi_{2pz}).
\end{align*}
\]

These bonds have a tetrahedral structure.\(^{15}\) Carbon has six electrons. The first two fill the 1s state. In one possible common configuration, the remaining four

\(^{14}\)It also neglects the change in the one-electron spectrum due to the magnetic effects of the “spin-orbit interaction.” We will return to this.

\(^{15}\)If the nucleus is at the center of a cube, these bonds point towards the corners (1, 1, 1), (−1, −1, 1), (1, −1, −1), and (−1, 1, −1), respectively.
electrons are placed one each in the four $sp^3$ orbitals. This accounts for the tetrahedral structure of the methane molecule, CH$_4$.

We can have four hybrid orbitals which include the $\phi_{2p_z}$ orbit and three orthogonal combinations, $sp^2$, of the orbits $\phi_{2s}$, $\phi_{2p_x}$, and $\phi_{2p_y}$ such as

$$\begin{align*}
\frac{1}{\sqrt{3}} \phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}} \phi_{2p_x} + 0 \phi_{2p_z} \\
\frac{1}{\sqrt{3}} \phi_{2s} - \frac{\sqrt{2}}{\sqrt{3}} \phi_{2p_x} + \frac{1}{\sqrt{2}} \phi_{2p_z} \\
\frac{1}{\sqrt{3}} \phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}} \phi_{2p_x} - \frac{1}{\sqrt{2}} \phi_{2p_z}
\end{align*}$$

(49)

The $sp^2$ hybrids have bonds at 120° in the $xy$ plane. As before, $\phi_{2p_z}$ has lobes above and below this plane. Thus, the following picture emerges for the binding of benzene, C$_6$H$_6$. Two electrons from each carbon atom occupy two of the $sp^2$ orbits and form a hexagon of carbon atoms. A third electron from each carbon sticks “out” of this hexagon and binds the six hydrogen atoms. The final electron from each carbon atom occupies the $2p_z$ orbital. These orbitals overlap strongly and allow these six electrons to move freely above and below the hexagon. Other aromatic hydrocarbons can be described in the same way. With incredible accuracy, one can approximate this motion as the motion of free particle on a “ring.”

Similar arguments with hybrid bonds allow us to consider the amazing structure of 60 carbon atoms. Imagine that each carbon atom has three bonds of identical length which lie (almost) in a plane. Sixty carbon atoms can form a perfect three-dimensional dodecahedron in which all carbon atoms are equivalent. Each atom is simultaneously at the vertices of two hexagons and one pentagon. This is exactly the form of a football. The remain valence electron is in a fourth orbit which is locally perpendicular to this plane and is free to roam all over the “football”. This atom is known as a “Bucky ball” or a “fullerene”. It was found experimentally a few years ago and has opened up a new branch of chemistry.
Chapter XI — Matrix Mechanics and Spin

In this chapter, we will consider an alternate formulation of quantum mechanics in terms of matrices (invented by Heisenberg.) Here, our energy eigenfunctions will come from the diagonalization of a matrix rather than from the study of boundary value differential equations. While this formulation is a little abstract, it is technically fairly easy. Once we have some experience with matrix mechanics, it will be natural to consider Pauli’s description of the spin (or intrinsic angular momentum) of the electron. This is a truly quantum mechanical problem (with no classical analogue!) which can only be treated using matrix methods.

The basics of matrix mechanics: We now imagine that we wish to describe wave functions by their expansion in any complete basis of states. As usual,

$$|\psi\rangle = \sum_n a_n |\phi_n\rangle .$$

(In principle, $n$ usually runs over an infinite range. In practice, this range will almost always be finite. We can express the effects of any operator, $\hat{F}$, simply as

$$\hat{F} |\psi\rangle = \sum_m b_m |\phi_m\rangle = \sum_m |\phi_m\rangle \langle \phi_m | \hat{F} |\phi_m\rangle a_n .$$

(1)

Clearly, we can express the relationship between the $a_n$ and $b_m$ through a simple matrix equation:

$$b_m = F_{mn} a_n$$

(2)

where

$$F_{mn} \equiv \langle \phi_m | \hat{F} |\phi_n\rangle .$$

(3)

In eqn.(3), I have used the convention, familiar from matrix algebra, of an implicit summation over a repeated index. If $\hat{F}$ is a Hermitian operator, the matrix $F_{mn}$ will be a Hermitian matrix with the property that

$$F_{mn} = F_{nm}^* .$$

Recall that all of the eigenvalues of a Hermitian matrix are real, and all of its eigenvectors are orthogonal. The eigenvalues and eigenfunctions of $\hat{F}$ now follow from the matrix eigenvalue equation

$$F_{mn} a_n = \lambda a_m .$$

(4)

Thus, quantum mechanics (as we have already learned it) can always be expressed as a matrix problem (but possibly one of infinite dimensions.) It is amusing to note that Schrödinger never learned anything about matrices. He never believed that matrix mechanics was equivalent to “his” quantum mechanics. Fortunately, you are smarter.

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16Simply take the inner product of this equation with $|\phi_m\rangle$.**
**Elementary matrix properties:** Matrices have the following properties:

- The product of two matrices has the simple form
  \[(AB)_{mn} = A_{mp}B_{pn}.\] (5)
  Evidently, \(AB\) is still a matrix.
- For any matrix, \(A\), there is (almost always\(^\text{17}\)) an inverse matrix, \(A^{-1}\), such that
  \[A^{-1}A = AA^{-1} = 1\] (6)
  where 1 is the “identity matrix”, \(1_{mn} = \delta_{mn}\).
- The transpose of a matrix simply involves the interchange of rows and columns. Thus,
  \[(A^T)_{mn} = A_{nm}.\] (7)
  A matrix is symmetric if \(A^T = A\).
- An element of the Hermitian adjoint of a matrix is the complex conjugate of the corresponding element in the transpose of the matrix. In other words,
  \[(A^\dagger)_{mn} = (A_{nm})^*.\] (8)
  A matrix is Hermitian if \(A^\dagger = A\).
- The scalar product of two vectors is simply
  \[\langle f|g \rangle = f^*_m g_m.\] (9)
  Evidently, we have summed over all indices. The result is a pure number.
- A matrix, \(U\), is unitary if
  \[U^\dagger = U^{-1}.\] (10)
- The trace of a matrix is the sum of its diagonal elements. Thus,
  \[\text{Tr} A = A_{mm}.\] (11)

**Unitary transformations in quantum mechanics:** Given eqn.(11), it is clear that the properties of a good basis (i.e., orthogonality and completeness) are preserved by making a unitary transformation of the matrix. For example, consider the transformation

\[|f'_m \rangle = U_{mn} |f_n \rangle\] (12)

with \(U\) unitary. If the states of the original basis, \(|f_n \rangle\), were complete, orthogonal, and normalized, the new states \(|f'_m \rangle\) will also have these properties. A change of basis states is thus always described by a unitary transformation. It

\(^{17}\) The inverse of a matrix exists unless the matrix has one or more zero eigenvalues.
is also clear that matrix operators must change their form when we change the basis. Thus

\[ \langle \phi | A | \psi \rangle = \langle \phi | U \dag (U H U \dag) U | \psi \rangle . \]  

(13)

We have done nothing more than insert two factors of 1. The term in parentheses represents the transformed operator, the remaining two factors represent the transformed bra and ket. Hence, under a unitary transformation,

\[ | \psi \rangle \rightarrow U | \psi \rangle \quad \text{and} \quad F \rightarrow UFU \dag . \]  

(14)

Since we have merely performed a passive transformation, we expect that a unitary transformation will not change the eigenvalues of a matrix. This is easily seen to be true. If we have

\[ F_{mn} a_n = \lambda a_m , \]

multiply the equation by \( U \) and insert 1 cleverly to obtain

\[ (UFU \dag)_{mn}(Ua)_n = \lambda (Ua)_m . \]

Thus, the eigenvalue is unchanged by a unitary transformation. Of course, the eigenfunction has changed. This was the point of the transformation!

**Angular momentum matrices:** Of course, we can now write the matrix corresponding to any operator in any basis we choose. It is simply a matter of work. The most interesting example is to write out the matrices corresponding to the operators for angular momentum, \( L_x \), \( L_y \), and \( L_z \) in the basis of states \( | \ell m \rangle \). Since all three of these operators commute with \( \hat{L}^2 \), these matrices are all diagonal in the quantum number \( \ell \). We need only consider these diagonal blocks. Evidently, the matrix for \( L_z \) is also diagonal in \( m \) with diagonal elements equal to \( \hbar m \). To do this, we first calculate the matrix elements of \( J_\pm \) using eqn.(30) from Chapter IX. This tells us that

\[ \langle jm' | J_\pm | jm \rangle = [(j \mp m)(j \pm m + 1)]^{1/2} \delta_{m' m\pm 1} . \]  

(15)

From the definitions \( J_\pm = (J_x \pm i J_y) \), we can immediately construct the desired matrices for any value of \( \ell \). Thus, we can write down the results for \( \ell = 1 \) as \( 3 \times 3 \) matrices:

\[ L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad \text{and} \quad L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} . \]  

(16)

For completeness, we can also write

\[ L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} . \]  

(17)

\footnote{I write “\( J \)” here to emphasize that these results do not care with the angular momentum is integer or half integer.}
Direct verification shows that these matrices satisfy the commutation relations

\[ [J_i, J_j] = i\hbar \epsilon_{ijk} \]

as they should. Similar matrices of dimension \((2\ell + 1)\) can be written down with equal ease for any value of \(\ell\). The same commutation relation will always be obeyed.

**Matrices for half-integer \(j\):** The above arguments were based solely on eqn.(30) of Chapter IX, which is valid for \(j\) both integer and half integer. We know that it is possible to write single valued functions only for the case of \(j\) integer. But nothing prevents us from writing the angular momentum matrices for half-integer \(j\).\(^{19}\) For \(j = 1/2\hbar\), we find the matrices

\[
J_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad J_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad J_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \]

It is easy to check that these matrices obey eqn.(19). Similarly, we can write similar results for other half-integer values of \(j\).

Note two special properties of the \(2 \times 2\) matrices of eqn.(20).\(^{20}\) These properties, which are easily verified by direct calculation, can be summarized in the anticommutator,

\[
\{J_i, J_j\} = \left(\frac{\hbar}{2}\right)^2 \delta_{ij}. \]

These results make it easy to verify a variety of very general results. (See below.)

**The Pauli spin matrices:** The matrices of eqn.(20) describing the angular momentum operators for spin \(\hbar/2\) can be written as

\[ J_i = \frac{\hbar}{2} \sigma_i \]

where the \(\sigma_i\) are known as the Pauli spin matrices. While the case of angular momentum \(\hbar/2\) cannot apply to orbital angular momentum, it can apply to some internal angular momentum (or “spin”) associated with elementary particles. Such an intrinsic spin represents a purely quantum mechanical effect without any classical analogue. In fact, we now know that electrons, protons, and neutrons all have an intrinsic spin \(s = \hbar/2\).\(^{21}\) This spin is described by the angular momentum operators of eqn.(20). Of course, all the usual commutation relations, such as eqn.(19), also apply to intrinsic spin. In addition to describing the spatial coordinates for such particles, we must also describe their spin wave

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\(^{19}\)The only thing that gives us pause is that we do not know what these matrices describe physically. Just wait for a couple of paragraphs!

\(^{20}\)These properties are special to spin \(1/2\) and are not shared by any other spin!

\(^{21}\)As usual, experiment came first and theory after. Stern and Gerlach did an experiment (see below) which showed that there was a missing quantum number for the electron. Pauli invented his matrices and the idea of intrinsic spin four years later in 1926.
function as being either spin “up” or “down.” These possibilities are described by a two-component column vector as
\[
\begin{pmatrix}
1 \\
0
\end{pmatrix}
\quad \text{and} \quad 
\begin{pmatrix}
0 \\
1
\end{pmatrix},
\]
respectively. Thus, for example, the wave function for an electron with momentum \(\hbar \mathbf{k}\) and spin up is
\[
\psi_+ = A e^{i \mathbf{k} \cdot \mathbf{r}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}.
\]

Let us how these spinors behave under rotations. We expect that the rotation operator,
\[
\hat{R}_\phi = \exp \left( i \mathbf{\hat{J}} \cdot \mathbf{\hat{J}} \right),
\]
will rotate a state by an angle \(\phi/|\mathbf{\phi}|\) about the axis \(\mathbf{\phi}/|\mathbf{\phi}|\). As usual, we interpret this operator through its Taylor series expansion. Using the specific properties of the Pauli matrices, we note that
\[
(\mathbf{\sigma} \cdot \mathbf{n})^2 = 1.
\]
Thus, the rotation matrix has the simple form
\[
\hat{R}_\phi = \cos \phi/2 + i (\mathbf{\sigma} \cdot \mathbf{n}) \sin \phi/2.
\]
Let us write this out explicitly for a rotation about the \(y\) axis:
\[
\hat{R}_\phi = \begin{pmatrix}
\cos \phi/2 & \sin \phi/2 \\
-\sin \phi/2 & \cos \phi/2
\end{pmatrix}.
\]
It is obvious that (i) this matrix is not Hermitean and (ii) it is unitary. Applying the rotation to a spin up state, we find
\[
\hat{R}_\phi \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix}
\cos \phi/2 \\
-\sin \phi/2
\end{pmatrix}.
\]
For the special case \(\phi = \pi\), we find the expected result that the spin up state is rotated into a spin down state. We can also perform the unitary transformation of the spin operators (or the Pauli matrices) under such rotations according to eqn.(15). We find that \(J_y\) is invariant under a rotation of \(\pi\) about the \(y\) axis. \(J_x\) is rotated into \(J_z\), and \(J_z\) is rotated into \(J_x\) under this transformation. Again, all is as it should be. Finally, we note that the spin up state is taken into minus itself under a rotation of \(2\pi\) (due to the presence of half angles.) This is the minus sign which caused all the problems with single valuedness of the wave functions for orbital angular momentum. It causes no such problems here.\(^{22}\)

*Magnetic moments — mostly classical:* According to the Biot-Savart Law, every electrical current produces a magnetic field. In particular, a small circular

\(^{22}\)Spinors are returned with a plus sign after a rotation of \(4\pi\) — two complete rotations.
loop of cross-sectional area $A$ carrying a current $I$ produces a magnetic dipole moment

$$\mu = IA .$$

(21)

The direction of the magnetic moment is perpendicular to the plane of the loop. If this current is produced by a charge moving in a circular orbit, it follows that the associated orbital magnetic moment is

$$\vec{\mu} = g \frac{e}{2mc} \vec{L}$$

(22)

where $e$ is the (negative) electron charge and the dimensionless “gyromagnetic ratio,” $g = 1$. If a magnetic moment is placed in a magnetic field, it feels a torque,

$$\mathbf{N} = \vec{\mu} \times \mathbf{B} ,$$

(23)

which causes the magnetic moment to align itself parallel to the magnetic field. Integrating this torque, we find a potential energy for a magnetic moment in a magnetic field of

$$V = -\vec{\mu} \cdot \mathbf{B} .$$

(24)

It is easy to see that there is no net force on a dipole in a uniform magnetic field (even though there is certainly a torque.) There is a net force on a dipole in an inhomogeneous field. This is given as

$$\mathbf{F} = -\nabla V = \nabla (\vec{\mu} \cdot \mathbf{B}) .$$

(25)

The intrinsic spin of the electron also produces a magnetic dipole moment. It is again proportional to $\mathbf{S}$ as in eqn.(23) with a $g$-factor of 2. Hence,

$$\vec{\mu} = \frac{e}{mc} \mathbf{S} = -\frac{|e| \hbar}{2mc} \vec{\sigma} .$$

(26)

The quantity $|e|\hbar/2mc$ is known as the “Bohr magneton.” The torque, potential, and force experienced by this intrinsic magnetic dipole moment are all given by the corresponding classical equations, eqns.(24)–(26).

The Stern–Gerlach experiment: In 1922 Stern and Gerlach performed an uncommonly clever experiment using a beam of silver atoms. Silver has 47 electrons. The first 46 fill shells completely and thus have an angular momentum (and a magnetic moment) of 0. The final electron is in a $5s$ state with $\ell = 0$. Hence, the total spin of silver is $\hbar/2$ and due to the intrinsic spin of this last electron.\(^{23}\) They sent their beam of silver atoms through a strongly inhomogeneous magnetic field with $\partial B_z/\partial z \neq 0$. According to eqn.(26), the magnetic force on the silver atoms was simply

$$F_z = \mu_z \frac{\partial B_z}{\partial z} .$$

(27)

\(^{23}\)Of course, Stern and Gerlach knew nothing about electron spin. They were about to discover it!
In other words, the magnitude and direction of the force depends on the orientation of $\vec{\mu}$. Stern and Gerlach knew that the silver atoms had a magnetic moment. Since their beam had been created by heating silver, they expected that their beam would contain random angular orientations of these moments. Hence, they expected that the distribution of the silver beam would simply be spread out after passing through the magnetic field. Instead of one “smeared” beam, they found two very sharp and well-separated beams (of equal intensity) corresponding to magnetic moments quantized as

$$\mu = \pm \frac{e\hbar}{2mc}. $$

We now understand that this is due to the quantization of the intrinsic spin angular momentum with allowed values of $S_z = \pm \hbar/2$. In effect, passing the beam through this inhomogeneous field was equivalent to a measurement of $S_z$. As expected (by us!), a measurement of $S_z$ can only return one of its eigenvalues.

They could have performed this experiment with a polarized beam of silver atoms. Imagine that that beam had been polarized with spin $+\hbar/2$ along the $x$ axis. From eqn.(20) we see that the corresponding spin eigenfunction is

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \left[ \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right]. \tag{28}$$

In other words, they would again have found the same results with equal amounts of spin up and down atoms.

**Precession of spin in a magnetic field:** Consider a free electron in a constant magnetic field, $B_z$. Assume that the spin function for the electron is initially

$$\xi(0) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}. $$

(In other words, the electron spin points along the positive $x$ axis.) We would like to find the spin function for later times. Hence,

$$\xi(t) = \frac{1}{\sqrt{2}} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}. \tag{29}$$

The Hamiltonian for this problem is

$$\hat{H} = -\vec{\mu} \cdot \vec{B} = \mu_b B_z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{30}$$

The time-dependent Schrödinger equation has the simple matrix form

$$\begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = -i\frac{\Omega}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ -b \end{pmatrix}. \tag{31}$$

\[\text{Since each orientation of the magnetic moment would feel a slightly different force and follow a slightly different trajectory.}\]
Here, $\Omega = |e| B_z / mc$, which is the Larmor or cyclotron frequency. Solution of this equation is simple and involves equating the upper and lower components of each side of this equation. (In this case, it involves separate, first-order equations for $a$ and $b$.) The solution is simply

$$\xi(t) = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp -i(\Omega/2)t \\ \exp +i(\Omega/2)t \end{pmatrix}.$$ (32)

Evidently, eqn.(30) agrees with the initial form of the wave function given above. By comparison with our discussion of the rotation operator above, we see that this wave function describes a spin wave function which is precessing (i.e., rotating) in the $xy$ plane with a frequency of $\Omega/2$.

**Eigenvalues and eigenfunctions of a spin in a constant magnetic field:** This problem is very similar to the precession problem — but much easier. We seek solution to the time-independent Schrödinger equation for a spin in a constant magnetic field, $B_z$.

$$\mu_B B_z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = E \begin{pmatrix} a \\ b \end{pmatrix}.$$ (33)

This equation is already diagonalized, so no solution is needed. The eigenfunctions are simply the eigenfunctions of $S_z$. The corresponding eigenvalues are simply $E = \pm \hbar \Omega/2$.

**Magnetic resonance:** We can put these previous results together to solve a really beautiful problem — magnetic resonance. Imagine that we have an electron in a constant magnetic field, $B_z = B_\parallel$. As we have just seen, there will be an energy difference of $\hbar \Omega_\parallel$ between spin up and spin down states. Now apply a weak magnetic field which rotates in the $xy$ plane with some frequency $\omega$:

$$B_x = B_\perp \cos (\omega t) \quad B_y = B_\perp \sin (\omega t).$$ (34)

As before, our Hamiltonian will be given as $\hat{H} = -\mu \cdot \mathbf{B}$. Our intuitive expectation is that it may be possible for the weak perpendicular field to induce transition between the spin up and spin down states. We expect that this transition will be most dramatic if we drive the system “on resonance.” Our expectations will be fulfilled! Simply writing out the time-dependent Schrödinger equation, we find the two equations

$$\frac{\partial a}{\partial t} = i(\Omega_\perp b e^{i\omega t} + \Omega_\parallel a)$$

$$\frac{\partial b}{\partial t} = i(\Omega_\perp a e^{-i\omega t} - \Omega_\parallel b).$$ (35)

These equations are coupled and not completely elementary to solve. (Note that we wish to impose the boundary conditions $a(0) = 1$ and $b(0) = 0$, which

\footnotetext[25]{Note that this is the first time we have encountered a problem where the Hamiltonian depends explicitly on time.}
correspond to the particle having spin up at $t = 0$.) One way (of many) to proceed is to solve the first of eqns.(35) for $b$ and to use this result in the second equation to get a single, second-order differential equation for $a$. This will lead to a general solution of the form

$$a(t) = \tilde{a}_1 \exp \left[ i (\omega/2 + \tilde{\omega}) t \right] + \tilde{a}_2 \exp \left[ i (\omega/2 - \tilde{\omega}) t \right].$$

(36)

Here $\tilde{a}_1$ and $\tilde{a}_2$ are arbitrary constant which can be set to satisfy the initial conditions. Further,

$$\tilde{\omega}^2 = \left( \Omega_{||} - \frac{\omega}{2} \right)^2 + \Omega_\perp^2.$$ 

(37)

Armed with the solution for $a(t)$, we can return and determine $b(t)$ from its formal solution. The result will have the form

$$b(t) = \tilde{b}_1 \exp \left[ -i (\omega/2 - \tilde{\omega}) t \right] + \tilde{b}_2 \exp \left[ -i (\omega/2 + \tilde{\omega}) t \right].$$

(38)

The constant $\tilde{b}_i$ is uniquely determined by the value chosen for $\tilde{a}_1$; $\tilde{b}_2$ is uniquely determined by $\tilde{a}_2$. Following through this tedious process, we finally obtain

$$
\begin{pmatrix}
  a(t) \\
  b(t)
\end{pmatrix} = \frac{\sin \tilde{\omega} t}{\tilde{\omega}^2} \left( e^{i(\omega/2)[i(\Omega_{||} - \omega/2) + \tilde{\omega} \cot \tilde{\omega} t]} \right). 
$$

(39)

So what does all this mean? First, there is a trivial check that we have not made mistakes. Taking the limit as $t \to 0$, we see that we have described a particle which is initially spin up. The probability of finding the particle in either spin state should be 1 for all $t$. A check of eqn.(39) reveals that

$$|a|^2 + |b|^2 = 1$$

for all $t$. Fine. The probability of finding a spin down state is

$$|b(t)|^2 = \frac{\Omega_\perp^2}{(\Omega_{||}^2 - \omega^2/4 + \Omega_\perp^2)} \sin^2 (\tilde{\omega} t).$$

(40)

Note that the factor in square brackets is time independent. In the special “on resonance” case of $\omega/2 = \Omega_{||}$ we see that this factor is 1. Thus, on resonance, we can flip the spin from up to down and back again as many times as we would like.

In practice, this experiment is performed on protons (which also have spin $\hbar/2$) instead of electrons. The magnetic moment of the water molecule is due to the intrinsic spins of the hydrogen nuclei (i.e., protons). We can place an object (e.g., a human patient) in a constant magnetic field $B_z$ to create $\Omega_{||}$. We can create the rotating field by feeding it with a radio frequency signal. When we go from the lower energy state to the higher, rf energy is absorbed from the field (and given back to the field when we make the transition from high to low
energy.) This absorbed energy can be measured and will be proportional to the local density of water molecules. In this manner, one can make body images.\footnote{The only small detail here is that our measurements are made at non-zero temperature. The energy difference between these states is roughly comparable to $kT$. Thus, both spin up and spin down states will be populated according to a Boltzmann factor. The lower energy state has a higher population by a factor of $\exp(-\Delta E/kT)$. Thus, on resonance, there will still be a net absorption of energy from the rf field.}

\textit{Addition of angular momentum:} All of the true things said in Chapter IX about the coupling of two angular momenta are true independent of whether these angular momenta are due to orbital motion or intrinsic spins. Following those arguments, we see (for example) that two independent spin 1/2 particles can either be described in the basis $|s_1 m_1 s_2 m_2\rangle$ or the basis of good total spin (and the $z$ component of total spin), $|s_1 s_2 SM\rangle$. It is easy to show that two electrons can have $S = 0$ or $S = \hbar$.

For future use, it is worth writing down the explicit form of the $S = 0$ wave function.

$$|S = 0M = 0\rangle = \frac{1}{\sqrt{2}} [ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] .$$

This state clearly has $S = 0$ since apply the spin raising operator to it will give 0. One important thing to notice here is that the form of this state is independent of our choice of basis. Since the total spin is 0, we can regard the single particle states appearing here as eigenfunctions of $\mathbf{n} \cdot \mathbf{S}$ where $\mathbf{n}$ is a unit vector in any direction. (This can be seen by applying the rotation operator to this states. The form will remain invariant.)

There is another example (which we shall study in greater detail in Chapter 12.) We can classify the orbital plus spin motion of a single electron in two ways. We can specify either $|\ell m_\ell m_s\rangle$ or we can specify the total angular momentum (i.e., orbital plus spin) and its $z$ component, $|\ell j m_j\rangle$. The techniques of Chapter IX allow us to go back and forth between these two bases. There is a very simple reason why the second basis is better for atoms. Imagine you are sitting on an electron in orbit around a nucleus. You see a rotating proton and, hence, a magnetic field. Your (electron) spin can interact with this spin to give rise to a magnetic term in the Hamiltonian which is proportional to $\mathbf{L} \cdot \mathbf{S}$. Such a term is called a “spin-orbit” interaction. Note that

$$\mathbf{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}})^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2 \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} . \tag{41}$$

The form of eqn.(41) indicates that we can diagonalize a Hamiltonian which includes a spin-orbit interaction trivially by working in the basis $|\ell j m\rangle$.

\textit{Bell's Inequality:} I want to deal with this fascinating topic in a manner quite different from Liboff. I want to tell you a story. I want to think about a very general classical experiment which is limited only by the idea of causality, and then I want to derive some results for this experiment (i.e., Bell’s inequality.) We shall then see how to make a quantum mechanical experiment with an identical in structure. The results of this experiment (which has been performed!) will
be seen to be in striking disagreement with some very basic classical ideas. First
the story.

Imagine that there are three men on three islands and that they can only
communicate by carrier pigeon. The man on the center island has a bag of
“instruction” cards. Each of the men on the other two has a measuring machine
with three switch settings — 1, 2, and 3 — which they control and two lights —
$R$ and $G$ — which show the results of the measurement. A sample instruction
card looks like this:

\[
[ 1R 2G 3R | 1G 2G 3R ]
\]

The man with the cards draws a card at random and tears it in half. He gives
each half to a carrier pigeon which flies off to one of the other two islands. The
instant before each pigeon lands, the men on these islands set their detector at
random to some position. The pigeon drops the card in the machine, and the
 correspon ding light lights. (In this case, if the man on the left island had set
his switch at 1, the red light would light.) I want to emphasize to points. First,
the experiment is completely causal. Each instruction card uniquely determines
which light will light for any setting of either machine. Second, the men with
the measuring devices can only communicate by carrier pigeon. There is no way
for to tell each other which switch settings they have chosen before the lights
go on. Each man notes the number of the trial and the color of the light which
lit. After a long series of these experiments, the men row back to the center
island and compare their lists. The question is: What is the probability that, in
any given trial, the same color light will light on the two devices? I emphasize
that this is a very general model of a classical experiment. It is completely
deterministic in the sense that the instructions give a unique outcome of the
experiment for every possible setting of the measurement devices. Further, the
two measurers cannot communicate. Hence, the outcome of one measurement
cannot possibly affect the other.

In general, there are evidently 64 kinds of instructions corresponding to the
$2^6$ possible choices of $R$ and $G$. For the experiment I have in mind, we will
imagine that there is a random mixture of instruction cards with the following
property: If the switches are the same on the two machines, the same lights
will go on. There are thus two instruction sets which look like

\[
[ 1R 2R 3R | 1R 2R 3R ]
\]

If such an instruction is selected, the probability of getting the same color light
is $P_{\text{same}} = 1$. There are another six instructions which look like

\[
[ 1R 2R 3G | 1R 2R 3G ]
\]

A little effort shows that the probability of getting the same color light in this
case is $P_{\text{same}} = 5/9$. No matter how we mix these two classes of instructions,
we see that

\[ P_{\text{same}} \geq \frac{5}{9}. \]

This is Bell’s inequality.
The quantum mechanical realization of this experiment is as follows. The instruction set is a pair of electrons in a state with \( S = 0 \). One electron is sent to each man (along the \( y \) axis.) The measuring devices are Stern-Gerlach experiments. The switches allow the field inhomogeneities to be rotated to 0, 120, and 240\(^\circ\) in the \( xz \) plane about the \( y \) axis parallel to the electrons’ direction of motion. For the man on the left, the red light will light whenever he measures an electron with spin up; for the man on the left, the red light will light when he measures a spin down electron. Given the explicit form of the \( S = 0 \) wave function described above, it is clear that they will always see the same light if they have the same switch settings. (That’s why I picked only those 8 instruction cards from the 64 which are possible.) The measuring devices are set only microseconds before the electrons arrive. The two devices are sufficiently far apart that a signal moving at the speed of light will not have enough time to send information about switch settings from one observer to another. All of this is just like our classical experiment above. However, quantum mechanical calculations and quantum mechanical experiments (!) show that the probability of getting the same color light is exactly 1/2.\(^{27}\) This violates Bell’s inequality.\(^{28}\)

The only way to view this result is that (somehow or other) measurement of the system at one point changed the wave function at a distant point which could not be reached by a signal travelling at the velocity of light (i.e., causally.) This suggests the extremely nasty idea that quantum mechanics might allow effects to come before causes\(^{29}\). Actually, the situation is not a total disaster. The men on the islands (and the men with the Stern-Gerlach devices) could only see this effect when they got together to compare the results. This means that no information is actually being sent at speeds faster than light. It does mean that Postulate II of quantum mechanics\(^{30}\) is very hard to understand. It is certainly hard (impossible?) to make this result consistent with our classical intuition regarding causal experiments. Some people think that such experiments reveal a fundamental defect in quantum mechanics which needs to be fixed. Others (including me) think that they reveal a defect in our interpretation of quantum mechanics which needs to be more subtle. Whichever view appeals to you, we can agree with the wise words of David Mermin: “Anybody who understands Bell’s inequality and isn’t worried has rocks in his head.”

Proving that \( P_{\text{same}} = 1/2 \): Let us prove this assertion. The two switch settings are the same with probability 1/3. In this case, the two Stern-Gerlach devices measure spin projections along the same axis. Given the explicit form of the \( S = 0 \) state (see above), we see that a measurement at one device of \( \uparrow \) ensures a measurement of \( \downarrow \) at the other. In other words, when the switches are

\(^{27}\)To keep the argument flowing along, I’ll save the proof of this fact to the next section.

\(^{28}\)These easiest experiments are carried out with polarized photons and polarization filters rather than with polarized electrons. The qualitative results are the same. Bell’s inequality is violated.

\(^{29}\)You would feel very uncomfortable in a world in which your finger burned before some idiot lit a match under it! So would I.

\(^{30}\)Which states that the measurement of \( A \) always returns an eigenvalue of \( \hat{A} \) and changes the wave function to the corresponding eigenfunction, \( \phi_a \).
the same, we get the same color light with probability 1. If the two switches are not the same, the devices measure spin projections onto axes with a relative rotation of 120°. (This will be the case 2/3 of the time.) Let one of these directions define the z axis. A measurement of \( \downarrow \) at this device ensures that the wave function for the other electron is

\[
\hat{R}_{\phi=2\pi/3} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos \pi/3 \\ -\sin \pi/3 \end{pmatrix} = \begin{pmatrix} 1/2 \\ -\sqrt{3}/2 \end{pmatrix}.
\]

The probability of measuring spin \( \uparrow \) (and, hence, getting the same color light) is 1/4. Obviously, an identical result applies if the first device measures an up spin. Combining these results, we obtain

\[ P_{\text{same}} = \frac{1}{3}(1) + \frac{2}{3}(1/4) = \frac{1}{2}. \]

This is what I claimed above. This result represents a clear violation of Bell’s inequality that \( P_{\text{same}} \geq 5/9 \).
— Chapter XII —

The Pauli Principle, Chemistry, Atoms, and Molecules

In this final chapter, we will deal with the Pauli Principle which asserts that the wave function for identical particles with half-integer spin must be antisymmetric under the interchange of the particles. This presents the final tool needed to explain the chemical properties of atoms. It will further enable us to deal with the rather specific problem of the binding of the hydrogen molecule, $H_2$.

The Pauli Principle: It is common to consider “identical” particles in classical mechanics, but identity is not really terribly serious. There is little difference between the classical behaviour of identical particles and that of “almost identical” particles. This is not the case in quantum mechanics where identical particles (e.g., electrons or protons or hydrogen atoms) are totally indistinguishable. The Hamiltonian must be invariant under the interchange of the labels of any two identical particles 1 and 2, $\mathcal{P}_{12}$. (Alternatively, we can interchange all of the quantum numbers of the two particles.) In other words,

$$[\hat{H}, \mathcal{P}_{12}] = 0 .$$

It is also evident that applying $\mathcal{P}_{12}$ twice does nothing to a wave function. Thus, $\mathcal{P}_{12}^2 = 1$, and the eigenvalues of the exchange operator can only be $\pm 1$. The corresponding eigenfunctions are evidently the symmetric and antisymmetric states

$$\phi_S(x_1, s_1; x_2 s_2) = +\phi_S(x_2, s_2; x_1 s_1) \quad \phi_A(x_1, s_1; x_2 s_2) = -\phi_A(x_2 s_2; x_1 s_1)$$

where $s$ stands for spin (and any other!) quantum numbers. Given eqn. (1), it is clear that the symmetry or antisymmetry of a wave function is true for all times no matter how the Hamiltonian may change with time. Thus, we prefer to associate the even- or oddness under particle exchange with the particles rather than the Hamiltonian.

Bosons, Fermions, and the Pauli Principle: Particles with integer intrinsic spin are known as bosons. Photons and $\pi$ mesons are examples of bosons. The wave function for a system will always be symmetric under the interchange of identical bosons. Particles with half-integer spin (e.g., electrons, protons, and neutrons) are called fermions. A wave function must always be antisymmetric under the interchange of identical fermions.

It is obvious from eqn. (2) that $\phi_A(x_1, s_1; x_2 s_2) = 0$. In other words, identical fermions with the same (z-component of) spin cannot be at the same place at the same time. Further, if our antisymmetric wave function has the form of a product, it is clear that

$$\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)$$

$\text{31} \text{You do not expect that your ability to play billiards will change if I change the color of the balls.}$
must be identically 0 if \( a = b \). (Here, “1” is short hand for the coordinates and spin of particle 1.) Thus, two identical fermions cannot be in the same state. This fact, stated in two ways, is an expression of the Pauli Principle.

Atoms again: Let us consider atoms again under the assumption that we can neglect electron-electron interactions. As noted in Chapter XI, there is a spin-orbit force due to the magnetic interaction between the intrinsic spin of the electron and the orbital magnetic moment of the proton (as viewed from the electron.) Thus, for non-interacting electrons, the best set of quantum number is \( |n\ell j_m\rangle \). The energy of these states is given (more or less) by the hydrogenic atom eigenstates plus a shift from the spin-orbit force. (The state with \( j = \ell - 1/2 \) is always of lower energy than the state of \( j = \ell + 1/2 \).) Due to the Pauli Principle and the fact that electrons are fermions, we can put at most one electron in each of these states. Note that we get a particularly stable (i.e., low energy) configuration when all of the possible states with a given value of \( n \) are filled. (Such configurations are known as “closed shells”. Let us take a quick walk through the start of the periodic table to see how this works.

- Hydrogen has one electron. One more would make a closed shell with \( n = 1 \). Its spin should be 1/2. (It is.) Hydrogen is prepared either to give up its electron (and make \( \text{H}^+ \) as in acids) or accept an electron (and make \( \text{H}^- \) as in hydrides.

- Helium has two electrons. It has a closed \( n = 1 \) shell. Its spin is 0 and it should be chemically inert. Both states are correct.

- Lithium has a closed shell plus one electron in the \( 2s \) state. Its spin is 1/2 and it forms \( \text{Li}^+ \) ions.

- Beryllium has two electrons in the \( 2s \) shell. Its spin is 0 and it forms \( \text{Be}^{++} \) ions.

We could go on like this! Let me end by noting that oxygen is two particle away from a closed shell, fluorine is one away, and neon has a closed \( n = 2 \) shell. Neon is a rare gas and chemically inert. Oxygen has valence \(-2\), and fluorine has valence \(-1\). Everything is consistent with our very simple picture!

Slater determinants: We usually assume that we can approximate wave functions for atomic electrons by using some “effective” central potential for non-interacting electrons. The total energy will then be the sum of the “single particle energies” of all of the electrons. Further, their wave functions can be written as antisymmetrized products of wave functions for the individual electrons. An easy way to do this is with a Slater determinant wave function defined as

\[
\phi_A(1, 2, \ldots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_{a1}(1) & \phi_{a2}(1) & \ldots & \phi_{aN}(1) \\
\phi_{a1}(2) & \phi_{a2}(2) & \ldots & \phi_{aN}(2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_{a1}(N) & \phi_{a2}(N) & \ldots & \phi_{aN}(N)
\end{vmatrix}.
\]
Since a determinant changes sign under the interchange of any two rows (or columns), it is clear that this wave function will change sign under particle exchange. It will vanish whenever two of the states are the same. Thus, such a wave function correctly incorporates the antisymmetry of identical fermions. If the states $\phi_{\alpha_j}$ are orthogonal and correctly normalized, the state $\phi_A$ is also normalized with

$$\langle \phi_A | \phi_A \rangle = 1 .$$

**The helium atom:** The helium atom has two (identical!) electrons moving in the field of the helium nucleus with charge $+2e$. We can write the Hamiltonian for this problem as

$$\hat{H} = \left( \frac{p_1^2}{2m} - \frac{2e^2}{r_1} \right) + \left( \frac{p_2^2}{2m} - \frac{2e^2}{r_2} \right) + \frac{e^2}{r_{12}} + \hat{H}_{SO} .$$

(4)

We recognize the first two terms as the Hamiltonians which would lead to the standard hydrogenic wave functions for each of the two electrons. We have also allowed for a possible spin-orbit interaction which will be discussed below. Of course,

$$r_{12} = |r_1 - r_2| .$$

As expected, eqn.(4) commutes with the particle interchange operator. The total spin of the two electrons can be $S = 0$ or $S = 1$. In order to make totally antisymmetric wave functions, these spin functions must be associated with symmetric and antisymmetric spatial wave functions. To start out, let us neglect both the spin orbit force and the repulsive interaction between the electrons. These spatial wave functions would then be

$$\phi_{S, A} = \frac{1}{\sqrt{2}} [\phi_{\nu_1(1)} \phi_{\nu_2(2)} \pm \phi_{\nu_1(2)} \phi_{\nu_2(1)}] \quad \nu_1 \neq \nu_2$$

$$\phi_S = \phi_{\nu_1(1)} \phi_{\nu_2(2)} \quad \nu_1 = \nu_2 = \nu .$$

(5)

Here, $\phi_\nu$ stands for the hydrogenic wave function with quantum numbers $n\ell m$. Our initial approximation for the energy of these states is simply

$$E_{n_{1n_2}, S, A} = -2mc^2 \alpha^2 \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right) + \Delta E_{n_{1n_2}, S, A} .$$

(6)

Without doing any work, it is clear that the states with $S = 1$ will have a lower energy than the states with $S = 0$. The triplet states have an antisymmetric spatial wave function which will reduce the probability that the two electrons will come close to each. This naturally gives a smaller contribution from the Coulomb repulsion between the electrons.\textsuperscript{32}

\textsuperscript{32}A similar argument applies for atoms with more electrons. Given the spatial wave functions to be filled, the lowest energy state will result from the spatial state with the largest degree of antisymmetry. The corresponding spin state will have the greatest degree of symmetry. In general, this will be realized by having the largest allowed total spin (consistent with the Pauli Principle.) This is known as "Hund’s first rule."
It is easy to calculate the expectation value of $\hat{H}$ using the wave functions of eqn.(5). We shall concern ourselves with relatively low energy excitations and keep one of the electrons in the ground state with $\nu = (100)$. Neglecting the spin-orbit force, we find

$$\Delta E_{(100\mid n\ell m)\text{S,A}} = A \pm B$$

with

$$A = \langle \phi_{100}(1)\phi_{n\ell m}(2)|\frac{e^2}{r_{12}}|\phi_{100}(1)\phi_{n\ell m}(2)\rangle$$

$$B = \langle \phi_{100}(1)\phi_{n\ell m}(2)|\frac{e^2}{r_{12}}|\phi_{100}(2)\phi_{n\ell m}(1)\rangle.$$  

For obvious reasons, these terms are called “direct” and “exchange” terms, respectively. These integrals can be evaluated either analytically or numerically. Even without evaluating them, it is not so far to show that they are both positive. Comparison with the experimental excitation energies of helium is really pretty good.

In the case of the states with $S = 1$, we can also include the effects of the spin-orbit force. This suggests that we should classify the states by $(\ell, J, M_J)$ with $J$ equal to $\ell - 1$, $\ell$ and $\ell + 1$. As we might expect, the spin-orbit force causes a small shift in the energy of these states. (The energy increases with increasing $J$.)

The helium ground state: Let us do this problem a little better. The normalized hydrogenic (spatial) wave functions for the ground state can be written out explicitly as

$$\phi = \left(\frac{Z^3}{\pi a_0^3}\right) \exp[-Z(r_1 + r_2)/a_0].$$

(Of course, this state is spatially symmetric. It necessarily corresponds to $S = 0$.) We might be tempted to set $Z = 2$ (since we are talking about helium) and be done with it. But wait a bit. The expectation value of the Hamiltonian is simply

$$\langle H \rangle = \frac{Z^2e^2}{a_0} - \frac{4Ze^2}{a_0} + \frac{5Ze^2}{8a_0}.$$  

The first two terms come from the hydrogenic part of the Hamiltonian. (We get the energy estimate of the leading term in eqn.(6) if we set $Z = 2$.) The final term is simply the expectation value of $e^2/r_{12}$. The way to calculate this integral is as follows. The charge distribution of particle 1 is spherically symmetric. Using Gauss’s law, it is easy to construct the electrostatic potential due to this charge density for any value of $r_2$. (Find the amount of charge due to $r_1$ inside $r_2$. The potential is the potential due to this amount of point charge at the origin.) The charge density of particle 2 interacts with this potential. The integral over $r_2$ is easy. (Work out the details yourself!)

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33I have ignored the single special case $(n\ell m) = (100)$. See the next paragraph.
Let us play a bit with eqn.(10). Simply inserting \( Z = 2 \) gives a ground state energy of \( -27/8(e^2/a_0) \). We can do better, however, if we regard \( Z \) as a parameter which can be varied to minimize the energy of the ground state. This yields \( Z = 27/16 \) and an energy of
\[
E_{\text{g.s.}} \approx - \left( \frac{27}{16} \right)^2 \frac{e^2}{a_0} .
\]
This is within 2% of the experimental ground state energy of \( = 2.904 \frac{e^2}{a_0} \). In effect, each electron partially screens (and thus reduces) the charge of the helium nucleus. Our variational parameter is obviously the “effective charge” of the helium nucleus. For excited states with large values of \( \ell \), the exchange term will be relatively small. Further, the ground state electron will almost always be inside \( r_2 \) and will thus screen one unit of the nuclear charge. For such states, it is a fairly good approximation to set \( Z = 1 \) and return to a spectrum which is very similar to that of the hydrogen atom itself.

**The hydrogen molecule:** To get a sense of what we can do (and how complicated it can get!), let us consider the diatomic hydrogen molecule. This system consists of two protons \((a \text{ and } b)\) and two electrons \((1 \text{ and } 2)\). The Hamiltonian is terribly complicated with kinetic energy operators for each of the four particles and six two-body interactions between the four charge particles. We can simplify things a little by noting that the protons are much heavier than the electrons so that we can set the proton momenta equal to 0 and keep the inter-proton distance \((r_{ab})\) as a constant which we can finally vary to minimize the energy. We will neglect the the spin of the electrons except for the fact that we insist that their wave function would obey the Pauli Principle. Let us write the Hamiltonian as
\[
\hat{H} = \left[ \frac{p_1^2}{2m} - \frac{e^2}{r_{1a}} \right] + \left[ \frac{p_2^2}{2m} - \frac{e^2}{r_{2b}} \right] + \frac{e^2}{r_{12}} - \frac{e^2}{r_{2a}} - \frac{e^2}{r_{1b}} + \frac{e^2}{r_{ab}} .
\]
(11)
The first term is the Hamiltonian for atom \( a \), and \( r_{1a} \) is the distance between electron 1 and proton \( a \). The second term is the Hamiltonian for atom \( b \), and \( r_{2b} \) is the distance between electron 2 and proton \( b \). The remaining terms are self-explanatory. I note only that the final term describes the interaction between the protons and will not be part of the quantum mechanical problem (since we assume the protons to be fixed.) It does contribute to the total molecular energy.

We can solve this problem approximately by keeping only the first two terms in eqn.(11) and approximating the wave function using only the hydrogenic ground state wave functions for atoms \( a \) and \( b \). The total electron spin can be \( S = 1 \). This spin state is symmetric, and thus the Pauli Principle requires that the corresponding spatial state must be antisymmetric. The total electron spin can be \( S = 0 \). As we saw in Chapter XI, this state is antisymmetric, and the corresponding spatial state must be symmetric. As usual, we write these states as
\[
\phi_{S,A} = \frac{1}{\sqrt{2}} \left[ \phi_a(1) \phi_b(2) \pm \phi_b(1) \phi_a(2) \right] .
\]
The idea is that $\phi_a$ and $\phi_b$ are just the usual hydrogenic ground state wave functions centered at $r_a$ and $r_b$, respectively. These wave functions serve as trial wave functions. As we have seen, the expectation values

$$\langle \phi_{S,A} | \hat{H} | \phi_{S,A} \rangle \approx E_{S,A}(r_{ab})$$  \hspace{1cm} (12)

provide an upper bound on the ground state energy of the molecular states with total spin $S = 0$ and $S = 1$, respectively. These expectation values are functions of the interproton spacing, $r_{ab}$.

It is now convenient to construct the “potential energy” experienced by the two hydrogen atoms by evaluating the expectation value of the full Hamiltonian less the energy of the two hydrogen atoms in their ground states,

$$V_{S,A}(r_{ab}) = \langle \phi_{S,A} | \hat{H} | \phi_{S,A} \rangle - 2 E_{g.s.}.$$  \hspace{1cm} (13)

All of the integrals can be performed analytically, but it is a very tedious business. The results can be summarized as follows. The state with $S = 1$ (and an antisymmetric spatial wave function) has a potential which is always positive as a function of $r_{ab}$. There is no binding. The state with $S = 0$ (and a symmetric spatial wave function) has a potential energy which is attractive at long distances with a minimum at about 1.5$\alpha_0$ (roughly 0.8 Å) of some −4 eV. At shorter distances, Coulomb repulsion dominates, and the potential is again positive. This state binds. The qualitative explanation of this phenomenon is clear. Any distortion of the hydrogenic wave functions tends to raise the energy. We can lower the energy only if there is a relatively large probability of finding both of the electrons in the region between the two protons. (In this region, there are two repulsive interactions — between the two electrons and between the two protons. The four electron-proton interactions are negative and win.) Evidently, there is a much greater probability of this favorable spatial distribution for $\phi_S$ than for $\phi_A$. Since protons are heavy (relative to electrons), this weak attractive potential is sufficient to bind the hydrogen molecule. The actual calculated binding energy (and interproton spacing) is fairly accurately estimated by this crude calculations with errors of roughly 20%.

Since both electrons are shared completely democratically by each of the protons, it is not useful to think of this as an ionic bond, i.e., H⁺H⁻. It is rather an example of the kind of “covalent” binding which dominates most of organic chemistry.

Once the two hydrogen atoms are bound (in the state with electron spin $S = 0$), we can think about the excitation spectrum of the hydrogen molecule.

**Vibrations of diatomic molecules:** In general, we can write the Hamiltonian for the two protons as

$$\hat{H}_{\text{osc}} - \hat{H}_{\text{CM}} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} + V(r).$$  \hspace{1cm} (14)

Here, $\mu$ is the reduced mass for the two protons which is $\mu = m_p/2$. We have removed the center of mass motion in eqn.(14). This motion, the free motion
of the molecule as a whole, is described by a plane wave as usual. Since the $V(r)$ has a minimum, we expect that the potential for the two protons will look like a harmonic oscillator problem for small changes in $r_{ab}$. The corresponding “spring constant” is $K \approx 10$ ev/Å$^2$. We can induce transitions between adjacent harmonic oscillator states through the absorption and emission of photons in the near infrared region. (Try to calculate $\hbar \omega_0$ and verify this!) Of course, this harmonic approximation breaks down for high excitation energies. The molecule will simply break apart rather than vibrate.

*Rotations of diatomic molecules:* There are much lower energy excitations available for the hydrogen molecule — it can simply rotate. Imagine that we are in the (radial) ground state, with $r$ roughly constant and at the minimum of the potential, $r \approx r_0$. Then, eqn.(14) simply becomes

$$\tilde{H}_{\text{nuc}} = \frac{\tilde{L}^2}{2I},$$

(15)

where the moment of inertia, $I = \mu r_0^2$. In this case, the eigenvalues are simply proportional to the eigenvalues of $\tilde{L}^2$ so that

$$E_\ell = \frac{\ell(\ell + 1)}{2I}.$$  

(16)

It is easy to evaluate the difference between the lowest two rotational energy levels in order to confirm that this energy spacing is roughly 100 times smaller than $\hbar \omega_0$. (Show this!) Transitions between such rotational states regarding the emission or absorption of infrared light.

*Ortho- and Para-hydrogen:* Protons are also identical particles with spin 1/2. They must obey the Pauli Principle, too. Hence, we construct states with total nuclear spin $S_{\text{nuc}} = 1$ (known as ortho hydrogen) and states with $S_{\text{nuc}} = 0$ (known as para hydrogen.)$^{34}$ Do not be confused about which spin we are talking about. Hydrogen molecules *always* have a total electron spin of $S_{\text{elc}} = 0$. Otherwise, the two atoms will not bind. Now we are talking about total nuclear spin. Clearly, states with $S_{\text{nuc}} = 1$ are symmetric under the interchange of the nuclear spins. They must have an antisymmetric spatial wave function. Similarly, states with $S_{\text{nuc}} = 0$ are antisymmetric under the interchange of the nuclear spins. They must have a symmetric spatial wave function. Now something sneaky happens: Rotating the molecule by $\pi$ about any axis perpendicular to $r_{AB}$ interchanges the protons. Under such a rotation, the spherical harmonic $Y_{\ell m} \rightarrow (-)^\ell Y_{\ell m}$. As a result of the Pauli Principle, ortho hydrogen (with $S_{\text{nuc}} = 1$) has only rotational states with $\ell$ even and para hydrogen (with $S_{\text{nuc}} = 0$) has only rotational states with $\ell$ odd. The indistinguishable nature of the protons has “killed” exactly half of the rotational states in each of the two spectra!

Similar things happen if we replace each of the two protons by a deuteron (i.e., a nuclear bound state of one proton and one neutron.) The spin of the deuteron

$^{34}$These are terrible names! Don’t blame me. Blame the chemists.
is 1, and it is thus a boson. The deuterium molecule, D₂, thus exists in states with total nuclear spin 2, 1, and 0. These states are even, odd, and even (respectively) under the interchange of the nuclear spin wave functions. (Construct these states explicitly and demonstrate this fact!) Since deuterons are bosons, their total wave function must be even under particle exchange. Hence, we can have ℓ even, odd, and even for these three nuclear spin states, respectively. Again, exactly half the states are missing! Finally, we note that we can make a molecule, HD, using one proton and one deuteron. Now, the total nuclear spin can be 1/2 or 3/2. But these particles are evidently distinguishable! The Pauli Principle does not apply, and we can have all integer values of ℓ for either spin state. Needless to say, this dramatic effect of identical particles on molecular spectra has been confirmed by experiment.